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Hisashi ISAKA : Docket No. 2002-0217A  
Serial No. 10/067, 369 : Group Art Unit 1712  
Filed February 7, 2002 : Examiner Robert E. Sellers  
CURING COMPOSITION

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**DECLARATION**

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Akiko KOJIMA, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the  
Japanese Priority Application No. 2001-53204, filed February 27, 2001.

I further declare that all statements made herein of my own knowledge are true  
and that all statements made on information and belief are believed to be true; and  
further that these statements were made with the knowledge that willful false  
statements and the like so made are punishable by fine or imprisonment, or both,  
under Section 1001 of Title 18 of the United States Code, and that such willful false  
statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 19th day of March, 2004.



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Akiko KOJIMA

(TRANSLATION)

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number: Patent Application No. 2001-53204  
[ ST.10/C]: [JP2001-53204]

Applicant(s): Kansai Paint Co., Ltd.

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Kozo OIKAWA

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[Document Name] Specification

[Title of the Invention] Curing Composition

[Claims]

[Claim 1] A curing composition comprising:

(A) a polymerizable cyclic structure-containing component

5 comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one polymerizable cyclic structure in a molecule,

(B) 0.01 to 5 parts by weight of a metal triflate per 100 parts by weight of the above component (A), and

10 (C) 0.1 to 250 parts by weight of water,

wherein the above polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average.

15 [Claim 2] The curing composition as set forth in Claim 1, wherein a metal in the metal triflate (B) is at least one metal selected from scandium, yttrium, lanthanoid series metals, actinoid series metals, magnesium, and zinc.

[Claim 3] The curing composition as set forth in Claim 1 or 2, wherein the polymerizable cyclic structure-containing component (A) is dispersed in water.

20 [Claim 4] A method for forming a cured coating film, comprising applying the curing composition as set forth in any of Claims 1 to 3 on a base material and curing it by heating.

[Claim 5] A method for forming a cured coating film, comprising applying the curing composition as set forth in any of Claims 1 to 3 on an uncured  
25 thermosetting colored layer and then curing it by heating.

[Detailed Description of the Invention]

[0001]

[Technical field to which the invention belongs]

30 The present invention relates to a water-containing curing composition which can form a three-dimensionally cross-linked matter having excellent characteristics such as a hardness and a gloss and which is suited particularly to a coating composition, and a method for forming a coating film

using the above composition.

[0002]

[Prior art and its problem]

5 A curing composition comprising an epoxy group-containing resin  
and a cationic polymerization catalyst has so far been known, and a coating  
composition comprising a specific epoxy group-containing resin and a heat  
latent cationic polymerization catalyst is disclosed in, for example, Japanese  
Patent Application Laid-Open No. 158580/1998. However, this composition  
involves the problems that it is liable to be influenced by humidity, so that the  
10 coating environment and the coating steps are restricted to a large extent.

[0003]

Also, known is a method in which cyclic ethers represented by an  
epoxy compound are subjected to ring-opening polymerization in a vessel using  
a Lewis acid and an onium salt as initiators to synthesize polyethers. Various  
15 initiators are researched in this polyether synthesis field, and disclosed in, for  
example, Japanese Patent Application Laid-Open No. 502531/1996 is a method  
in which cyclic ethers are subjected to polymerization using a metal triflate,  
which is a Lewis acid, to synthesize polyethers.

[0004]

20 Further, it is described in U.S. Patent No. 3,842,019 and Polymer,  
Vol. 41, p. 8465 to 8474, 2000 that a cured matter is obtained by combining a  
multifunctional epoxy compound with a metal triflate.

[0005]

On the other hand, when a curing composition is an organic solvent  
25 diluting type, involved therein is a problem on global environmental protection  
caused by volatilization of organic solvents, and therefore, a water diluting type  
curing composition which is suited to global environmental protection is required  
to be developed.

[0006]

30 An object of the present invention is to obtain a water-containing  
curing composition which is less liable to be influenced by coating environment  
and coating conditions, excellent in curing property at a relatively low curing  
temperature without using a lot of a polymerization catalyst, and capable of

obtaining a cured matter excellent in hardness and physical and chemical performances.

[0007]

[Means to solve the problems]

5                   Intensive researches repeated by the present inventors in order to achieve the object described above have resulted in finding that a curing composition for the object can be obtained by using a specific metal triflate which is a Lewis acid as a cationic polymerization catalyst for a polymerizable cyclic structure-containing component, and they have come to complete the  
10 present invention.

[0008]

That is, the present invention provides a curing composition comprising:

                  (A) a polymerizable cyclic structure-containing component  
15 comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one polymerizable cyclic structure in a molecule,

                  (B) 0.01 to 5 parts by weight of a metal triflate per 100 parts by weight of the above component (A), and

20                   (C) 0.1 to 250 parts by weight of water,

wherein the above polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average.

25 [0009]

Also, the present invention provides a method for forming a cured coating film in which the curing composition described above is applied on a base material and cured by heating.

[0010]

30                   Further, the present invention provides a method for forming a cured coating film in which the curing composition described above is applied on an uncured thermosetting colored layer and then cured by heating.

[0011]

The water-containing curing composition and the method for forming a cured coating film according to the present invention shall be explained below in detail.

[0012]

5 [Mode for carrying out the invention]

At first, a curing composition of the present invention shall be explained below in detail.

The curing composition of the present invention comprises the polymerizable cyclic structure-containing component (A) and the metal triflate  
10 (B) each described below as essential components.

[0013]

Polymerizable cyclic structure-containing component (A)

The polymerizable cyclic structure-containing component (A) in the composition of the present invention comprises a compound (a-1) having at  
15 least two polymerizable cyclic ether structures in a molecule or is a mixture of the above compound (a-1) and a compound (a-2) having one polymerizable cyclic structure in a molecule.

[0014]

A compound having the polymerizable cyclic ether structure in the  
20 above compound (a-1) includes oxiranes, oxetanes, oxolanes, oxepanes, and a cyclic formal such as dioxolanes and trioxanes, which have at least two polymerizable cyclic ether structures in a molecule.

[0015]

Further, capable of being given as a compound having the  
25 polymerizable cyclic structure in the above compound (a-2) are cyclic ethers including oxiranes, oxetanes, oxolanes, oxepanes, and a cyclic formal such as dioxolanes and trioxanes, and in addition thereto, cyclic esters (lactone), cyclic amides (lactam), and cyclic iminoethers, which have one polymerizable cyclic structure in a molecule.

30 [0016]

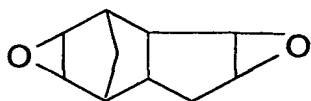
A compound in which a cyclic ether structure equivalent falls in a range of 70 to 3,000; preferably 80 to 1,500 is suitably used as the compound (a-1) described above.

[0017]

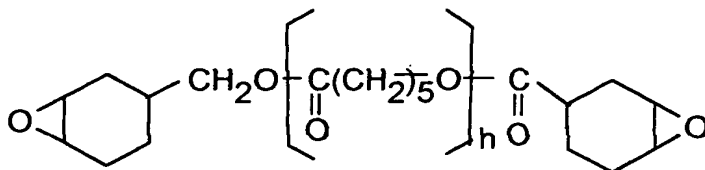
Among the compounds (a-1), capable of being given as the oxiranes are, for example, compounds having two or more epoxy groups such as dicyclopentadiene dioxide,

- 5 (3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexanecarboxylate, bis(2,3-epoxycyclopentyl) ether, bis(3,4-epoxycyclohexylmethyl) adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, (3,4-epoxy-6-methylcyclohexyl)methyl-3,4-epoxy-6-methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl) acetal,
- 10 bis(3,4-epoxycyclohexyl) ether of ethylene glycol, 3,4-epoxycyclohexanecarboxylic acid diester of ethylene glycol, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane, Celoxide 2080 (trade name, difunctional epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), Epolead GT300 (trade name, trifunctional alicyclic epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), Epolead GT400
- 15 (trade name, tetrafunctional alicyclic epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), Celoxide 3000 (trade name, difunctional epoxy compound, manufactured by Daicel Chemical Industries, Ltd.), EHPE (trade name, multifunctional epoxy resin, manufactured by Daicel Chemical Industries, Ltd.), compounds represented by the following formulas:
- 20

[0018]

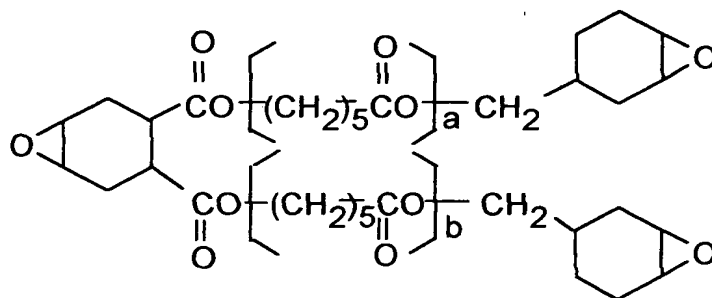


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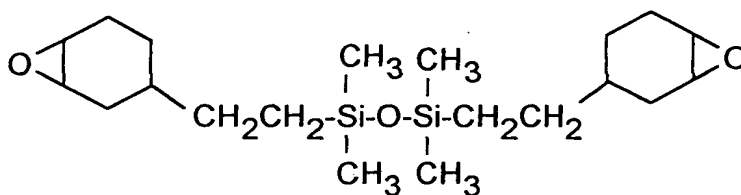
30

(h is an integer of 1 or more)



(a and b are an integer of 0 or more)

[0019]



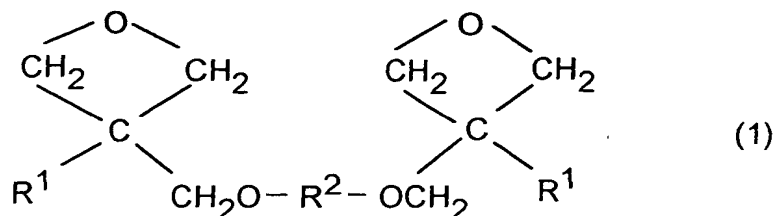
[0020]

ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin diglycidyl ether, polyglycerin polyglycidyl ether, trimethylolpropane polyglycidyl ether, pentaerythritol polyglycidyl ether, spiro glycol diglycidyl ether, 2,6-diglycidyl phenyl ether, sorbitol polyglycidyl ether, triglycidyl isocyanurate, bisphenol A diglycidyl ether, butadiene dioxide, diglycidyl phthalate, diglycidyl tetrahydrophthalate, vinylcyclohexene dioxide, limonene dioxide, bisphenol A epoxy resins, cresol novolak epoxy resins, and epoxyphenol novolak resins; polymers of epoxy group-containing polymerizable unsaturated monomers such as glycidyl (meth)acrylate, methylglycidyl (meth)acrylate, allyl glycidyl ether, 3,4-epoxycyclohexylmethyl (meth)acrylate, caprolactone-modified compounds of 3,4-epoxy-cyclohexylmethyl (meth)acrylate, and 3,4-epoxyvinylcyclohexane; and copolymers of the above epoxy group-containing polymerizable unsaturated monomers with other copolymerizable monomers. In the present invention, "(meth)acrylate" means acrylate or methacrylate.

[0021]

Among the compounds (a-1), capable of being given as the oxetanes is, for example, a compound represented by the following formula (1):

[0022]



[0023]

(In the above formula, two R<sup>1</sup>'s may be the same or different and mean the same as described previously; and R<sup>2</sup> represents an alkylene group having 1 to 6 carbon atoms, a cycloalkylene group, a phenylene group, a xylylene group, or a polyalkyleneoxy group having 4 to 30 carbon atoms.)

[0024]

Among the compounds (a-1), capable of being given as the compound having both oxiranes and oxetanes are 3-ethyl-3-(3,4-epoxycyclohexylmethyl)oxymethyloxetane and 3-ethyl-3-glycidyloxymethyloxetane.

[0025]

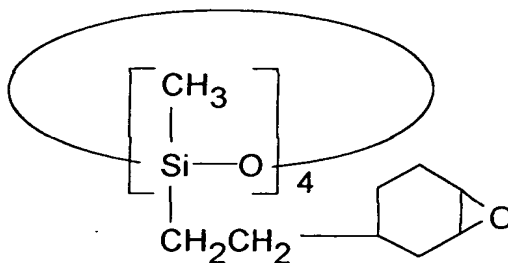
Capable of being suitably used as the compound (a-2) having one polymerizable cyclic structure in a molecule is a compound in which a polymerizable cyclic structure equivalent falls in a range of 70 to 1,000, preferably 80 to 500.

[0026]

Among the compounds (a-2), capable of being given as the cyclic ethers are, for example, oxiranes such as glycidol, styrene oxide, alkyl monoepoxide, phenyl glycidyl ether, alkyl monoglycidyl ether, Cardura E10 (manufactured by Shell Chemicals), Glydex N10 (trade name, manufactured by Exxon Co., Ltd.), alkyl glycidyl esters including Araldite PT910 (trade name, manufactured by Ciba-Geigy Co., Ltd.), glycidyl (meth)acrylate, methylglycidyl (meth)acrylate, allyl glycidyl ether, 3,4-epoxycyclohexylmethyl (meth)acrylate, caprolactone-modified products of 3,4-epoxycyclohexylmethyl (meth)acrylate, 3,4-epoxyvinylcyclohexane, cyclohexene oxide, α-pinene oxide, (3,4-epoxycyclohexyl)methyl alcohol, (3,4-epoxycyclohexyl)ethyltrimethoxysilane, and compounds represented by the following formula:

[0027]

5



[0028]

- 10 oxetanes such as 3-ethyl-3-methoxymethyloxetane,  
 3-ethyl-3-ethoxymethyloxetane, 3-ethyl-3-butoxymethyloxetane,  
 3-ethyl-3-hexyloxymethyloxetane, 3-methyl-3-hydroxymethyloxetane,  
 3-ethyl-3-hydroxymethyloxetane, 3-ethyl-3-allyloxymethyloxetane,  
 3-ethyl-3-(2'-hydroxyethyl)oxymethyloxetane,  
 15 3-ethyl-3-(2'-hydroxy-3'-phenoxypropyl)oxymethyloxetane,  
 3-ethyl-3-(2'-hydroxy-3'-butoxypropyl)oxymethyloxetane,  
 3-ethyl-3-(2'-butoxyethyl)oxymethyloxetane, 3-ethyl-3-benzyloxymethyloxetane,  
 3-ethyl-3-(p-tert-butylbenzyloxymethyl)oxetane,  
 3-ethyl-3-methacryloyloxymethyloxetane, and  
 20 3-ethyl-3-acryloyloxymethyloxetane; oxolanes such as tetrahydrofuran and  
 tetrahydrofurfuryl alcohol; oxepanes such as oxepane; dioxoranes such as  
 1,3-dioxorane; and trioxoranes such as 1,3,5-trioxorane.

[0029]

- The cyclic esters (lactone) include  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  
 25  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, enanthlactone, 3-methyl- $\beta$ -propiolactone,  
 3-methyl- $\gamma$ -butyrolactone, 3-methyl- $\delta$ -valerolactone, 3-methyl- $\epsilon$ -caprolactone,  
 4-methyl- $\epsilon$ -caprolactone, and 3,3,5-trimethyl- $\epsilon$ -caprolactone.

[0030]

- The cyclic amide (lactam) includes azetidinone, pyrrolidone, and  
 30  $\epsilon$ -caprolactam.

[0031]

The cyclic iminoethers include oxazoline and oxazine.

[0032]

These compounds having a polymerizable cyclic structure can be used alone or in combination of two or more kinds thereof.

[0033]

The polymerizable cyclic structure-containing component (A) has a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000, particularly 120 to 700 on average. The blending proportions of the compound (a-1) and the compound (a-2) each described above in the polymerizable cyclic structure-containing component (A) are preferably in the following ranges based on 100 parts by weight of the total of the both compounds from the viewpoint of a curing property:

Compound (a-1): 20 to 100 parts by weight, preferably 40 to 100 parts by weight

Compound (a-2): 0 to 80 parts by weight, preferably 0 to 60 parts by weight

[0034]

#### Metal triflate (B)

A metal triflate which is the (B) component of the composition of the present invention functions as a cationic polymerization catalyst for the polymerizable cyclic structure-containing component (A) and is a trifluoromethanesulfonic acid metal salt. As described above, it is known that a polymerizable cyclic structure-containing compound can be polymerized and three-dimensionally cross-linked by using a metal triflate as a cationic polymerization catalyst.

[0035]

On the other hand, a metal triflate is known as a Lewis acid which is relatively stable in water, and it is known as well that metals of particularly the 3 group in the periodic table and specific metals are stable in water (refer to O. Kobayashi, J. Am. Chem. Soc., 120, p. 8287 to 8288, 1998).

[0036]

At least one metal selected from metals of the 3 group in the periodic table, magnesium, and zinc is suited as a metal of the metal triflate described above from the viewpoint of a curing property, coloring, and a pot life. The

metal of the 3 group in the periodic table includes scandium, yttrium, lanthanoid series metals, and actinoid series metals. Among them, zinc is suited as the metal of the metal triflate. These metal triflates can be used alone or in combination of two or more kinds thereof.

5 [0037]

In the present invention, the blending amount of the metal triflate (B) falls suitably in a range of 0.01 to 5 parts by weight, particularly 0.05 to 2 parts by weight per 100 parts by weight of the polymerizable cyclic structure-containing component (A) described above from the viewpoints of the curing property and less liability of coloring of the cured matter.

10 [0038]

Water is present in the composition of the present invention, and in general, the metal triflate is dissolved in water. A content of water in the composition of the present invention falls suitably in a range of 0.1 to 250 parts by weight, particularly 1 to 100 parts by weight per 100 parts by weight of the polymerizable cyclic structure-containing component (A) described above.

15 [0039]

The metal triflate is readily dissolved in water, and also, it is relatively stable in water as described above and is hard to be hydrolyzed. Further, a catalytic activity in polymerization reaction is reduced when water is present. Therefore, the curing composition of the present invention is remarkably good in storage properties. The curing composition is heated in curing to volatilize water, whereby the component is advanced in polymerization reaction and cured.

20 [0040]

In the curing composition of the present invention, the polymerizable cyclic structure-containing component (A) may be dispersed in water. In this case, a dispersion aid such as an emulsifier, a dispersant, and a suspension stabilizer can be used in order to disperse the polymerizable cyclic structure-containing component. These emulsifier, dispersant, and suspension stabilizer shall not specifically be restricted and include, for example, emulsifiers, dispersants, and suspension stabilizers of an anionic type, a cationic type, a nonionic type, an anionic-nonionic type, and a zwitter-ionic type, and those of a

nonionic type, an anionic type, and an anionic-nonionic type are particularly desired.

[0041]

5       The curing composition of the present invention comprises as essential components, the polymerizable cyclic structure-containing component (A), the metal triflate (B), and the water (C) each described above and can comprise, if necessary, an organic solvent, a reactive diluent, a pigment, a UV absorber, a surface controller, an antioxidant, a fluidity controller, and a wax.

[0042]

10       A stirrer making use of shearing at a high speed such as a homogenizer can be used to disperse the curing composition in water. When the curing composition has a high viscosity and is hard to be dispersed, a solvent is added thereto to reduce the viscosity and disperse, and then, the solvent is removed, whereby a curing composition which is dispersed in water  
15       can be prepared. A procedure for dispersing includes a method in which the curing composition is added to an aqueous solution, in which a suspension stabilizer is dissolved in water in advance, and dispersed, or a method in which a suspension stabilizer is blended with the curing composition and then water is added to disperse them.

20       [0043]

      A method for forming a cured coating film of the present invention (a first production method) is a method to form a cured coating film by applying the curing composition described above on a base material and heating to cure. The base material shall not specifically be restricted to use as long as the above  
25       curing composition can be applied and it has a heat resistance for with standing heating to cure. Roll coating, curtain flow coating, and spray coating can be given as a coating means therefor.

[0044]

      The above curing composition is usually applied so that the coating  
30       film thickness falls in a range of about 2 to about 80  $\mu\text{m}$  in terms of a dried coating film thickness. A suitable baking condition thereof is that a material-reaching temperature usually falls in a range of 50 to 220°C.

[0045]

A method for forming a cured coating film of the present invention (a second production method) is a method to form a cured coating film by applying the above curing composition on an uncured thermosetting colored layer by wet-on-wet and then heating to cure.

5 [0046]

To be specific, this second production method includes, for example, a 2-coating 1-baking method in which the curing composition described above is used as a coating composition for forming a clear layer to apply the above curing composition on an uncured thermosetting colored layer (wet-on-wet  
10 coating) and bake them, and a 3-coating 1-baking method in which the above curing compositions are applied in order (wet-on-wet coating) for a first colored layer, a second coating layer, and a clear layer to bake them at the same time. These methods are merely examples, and the uncured thermosetting colored layer shall not be restricted to a coating and an ink. The method for forming a  
15 cured coating film of the present invention includes a method for applying the above curing composition on the uncured (including semi-cured) colored layer and heating to cure. For example, if the colored layer may be formed by carrying out removal of water and a solvent and semi-curing at a pre-heating step usually carried out in a water-based coating material, it is not deviated from  
20 the category of the second production method described above. Further, the uncured thermosetting colored layer may not be cured alone by itself and can be cured by transfer of a curing agent from a layer coated thereon.

[0047]

In the second production method described above, the same  
25 substrates that can be used in the first production method described above can be used as well. Among them, for example, materials such as car bodies, car parts, home electric appliances, cans for beverages, and metal sheets can be suitably coated. Further, the coating procedure, the coating film thickness, and the baking condition can also be the same as those in the first production  
30 method described above.

[0048]

[Examples]

The present invention shall further specifically be explained below

with reference to examples, but the present invention shall not be restricted only to these examples. "Parts" is based on weight.

[0049]

Synthetic Example 1: synthesis of an acrylic suspension stabilizer solution (a)

5           A reactor equipped with a stirrer, a condenser, a  
temperature-controlling device, a nitrogen-introducing tube, and a dropping  
funnel was charged with 65 parts of n-butanol. The reactor was substituted in  
an inside thereof with nitrogen, heated, and maintained at 110°C. Added drop  
by drop thereto in 3 hours was a mixture comprising 20 parts of RMA-450M  
10 (polyethylene oxide [45 monomer unit polymer] methacrylate, manufactured by  
Nippon Nyukazai Co., Ltd.), 10 parts of 2-hydroxyethyl acrylate, 20 parts of  
n-butyl acrylate, 30 parts of styrene, 10 parts of acrylic acid, 10 parts of  
2-ethylhexyl acrylate, and 2 parts of 2,2'-azobis(2-methylbutyronitrile). After  
finishing dropping, the solution was aged for 30 minutes, and the mixture of 0.5  
15 part of 2,2'-azobis(2-methylbutyronitrile) and 10 parts of n-butanol was further  
added drop by drop thereto in one hour. Then, the solution was aged for 30  
minutes, followed by neutralizing the solution in 0.7 equivalent with  
dimethylethanolamine and adding thereto deionized water to dilute the solution  
until the resin concentration became 30% by weight, whereby an acrylic  
20 suspension stabilizer solution (a) was obtained.

[0050]

Synthetic Example 2: synthesis of an oxirane ring-containing acrylic resin mixed  
solution (b-1)

25           A reactor equipped with a stirrer, a condenser, a  
temperature-controlling device, a nitrogen-introducing tube, and a dropping  
funnel was charged with 650 parts of Celoxide 2021P (trade name, difunctional  
epoxy compound, epoxy equivalent: about 130, manufactured by Daicel  
Chemical Industries, Ltd.). The reactor was substituted in an inside thereof  
with nitrogen, heated, and maintained at 165°C. Added drop by drop thereto in  
30 4 hours was a mixture comprising 50 parts of styrene, 150 parts of n-butyl  
acrylate, 75 parts of 2-ethylhexyl acrylate, 75 parts of 2-hydroxyethyl acrylate,  
150 parts of glycidyl methacrylate, and 50 parts of  
2,2'-azobis(2-methylbutyronitrile). After finishing dropping, the solution was

aged for 30 minutes, and the mixture of 2.5 parts of 2,2'-azobis(2-methylbutyronitrile) and 25 parts of Celoxide 2021P was further added drop by drop thereto in one hour. Then, the solution was aged for 30 minutes, whereby obtained was a mixed solution (b-1) of an acrylic resin and Celoxide 2021P having a non-volatile content of 94% and a Gardner viscosity (20°C) of X<sup>+</sup>. The acrylic resin (solid matter) contained in the resulting mixed solution (b-1) had a hydroxyl group value of 72 mg KOH/g, a number average molecular weight of 1510, and a weight average molecular weight of 2330.

[0051]

- 10 Synthetic Example 3: synthesis of an oxetane ring-containing acrylic resin mixed solution (b-2)

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube, and a dropping funnel was charged with 650 parts of Celoxide 2021P, and the reactor was substituted in an inside thereof with nitrogen, heated, and maintained at 165°C. Added drop by drop thereto in 4 hours was a mixture comprising 50 parts of styrene, 150 parts of n-butyl acrylate, 75 parts of 2-ethylhexyl acrylate, 75 parts of 2-hydroxyethyl acrylate, 150 parts of 3-ethyl-3-methacryloyloxymethyloxetane, and 50 parts of 2,2'-azobis(2-methylbutyronitrile). After finishing dropping, the solution was aged for 30 minutes, and the mixture of 2.5 parts of 2,2'-azobis(2-methylbutyronitrile) and 25 parts of Celoxide 2021P was further added drop by drop thereto in one hour. Then, the solution was aged for 30 minutes, whereby obtained was a mixed solution (b-2) of an acrylic resin and Celoxide 2021P having a non-volatile content of 94% and a Gardner viscosity (20°C) of Y. The acrylic resin (solid matter) contained in the resulting mixed solution (b-2) had a hydroxyl group value of 72 mg KOH/g, a number average molecular weight of 1440, and a weight average molecular weight of 2190.

[0052]

- 30 Synthetic Example 4: synthesis of an acrylic resin aqueous dispersion (c-1)

A reaction vessel was charged with 140 parts of deionized water, 2.5 parts of "Newcol 707SF" (trade name, surfactant, solid content: 30%, manufactured by Nippon Nyukazai Co., Ltd.), and 80 parts of the following monomer mixture (1). They were stirred and mixed in nitrogen flow, and a

monomer emulsion comprising 4 parts of 3% ammonium persulfate and 42 parts of deionized water was added to the reaction vessel at 60°C in 4 hours by means of a constant flow pump. After finishing addition, the solution was aged for one hour.

5 Monomer mixture (1)

	Methyl methacrylate	55 parts
	Styrene	10 parts
	n-Butyl acrylate	9 parts
	2-Hydroxyethyl acrylate	5 parts
10	Methacrylic acid	1 part

[0053]

Next, the reaction vessel described above was maintained at 80°C in an inside thereof, and 20.5 parts of the following monomer mixture (2) and 4 parts of 3% ammonium persulfate were added drop by drop to the reaction vessel at the same time in 1.5 hours. After finishing addition, the solution was aged for one hour and then filtered through a nylon cloth of 200 mesh at 30°C. Deionized water was further added thereto, and the pH was controlled to 7.5 with N,N-dimethylaminoethanol, whereby obtained was an acrylic resin aqueous dispersion (c-1) having an average particle diameter of 0.1  $\mu\text{m}$ , a Tg (glass transition temperature) of 46°C, and a non-volatile content of 20%.

20 Monomer mixture (2)

	Methyl methacrylate	5 parts
	n-Butyl acrylate	7 parts
	2-Ethylhexyl acrylate	5 parts
25	Methacrylic acid	3 parts
	"Newcol 707SF"	0.5 part

[0054]

Synthetic Example 5: synthesis of an acrylic resin aqueous solution (c-2)

A reaction vessel was charged with 60 parts of ethylene glycol monobutyl ether and 15 parts of isobutyl alcohol and heated to 115°C in nitrogen flow. After the temperature reached 115°C, added in one hour were 26 parts of n-butyl acrylate, 47 parts of methyl methacrylate, 10 parts of styrene, 10 parts of 2-hydroxyethyl methacrylate, 6 parts of acrylic acid, and the mixture

of one part of azobisisobutyronitrile and 5 parts of ethylene glycol monobutyl ether. The solution was aged for 30 minutes and then filtered through a nylon cloth of 200 mesh at 50°C to obtain a reaction product solution having a viscosity of Z<sub>4</sub> (Gardner bubble viscometer) and a non-volatile content of 55%.

- 5 The reaction product (solid matter) had an acid value of 47 mg KOH/g and a T<sub>g</sub> of 40°C. The reaction product solution was neutralized with dimethylaminoethanol in an equivalence, and deionized water was further added, whereby an acrylic resin aqueous solution (c-2) having a non-volatile content of 50% was obtained.

10 [0055]

#### Example 1

- Blended were 10 parts of the 30% acrylic suspension stabilizer solution (a) obtained in Synthetic Example 1, 37 parts of ion-exchanged water, 100 parts of Celoxide 2021P, and 0.5 part of zinc triflate, and they were mixed  
15 at 17,000 rpm for 10 minutes by means of a homogenizer, whereby a water-based curing composition having a non-volatile content of about 70% was obtained.

[0056]

#### Examples 2 to 13

- 20 The respective curing compositions were obtained in the same manner as in Example 1, except that components shown in the following Table 1 were used.

[0057]

#### Comparative Example 1

- 25 Zinc borofluoride [Zn(BF<sub>4</sub>)<sub>2</sub>] which was conventional as a cationic polymerization catalyst was used as a curing catalyst to prepare and evaluate a curing composition in the same manners.

[0058]

In Table 1, codes shown below mean the following:

- 30 Zn(OTf)<sub>2</sub> : zinc triflate  
Mg(OTf)<sub>2</sub> : magnesium triflate  
Yb(OTf)<sub>3</sub> : ytterbium triflate  
Gd(OTf)<sub>3</sub> : gadolinium triflate

Newcol 504(25) : trade name, 25% aqueous solution of polyoxyethylene nonylphenyl ether, manufactured by Nippon Nyukazai Co., Ltd.

5 Newcol 562SF : trade name, 60% solution of polyoxyethylene nonylphenyl ether sulfuric acid ester ammonium salt, manufactured by Nippon Nyukazai Co., Ltd.

[0059]

The respective curing compositions obtained in Examples 1 to 13 and Comparative Example 1 each described above were tested for a curing  
10 property, a coating film hardness, and coloring of the coating films based on the following test methods. The test results thereof are shown in the following Table 1.

#### Test methods

Curing property: the curing composition was applied on a tin plate by means of  
15 an applicator so that the cured thickness was about 45  $\mu\text{m}$  and heated and dried at the respective temperatures of 100°C, 120°C, and 140°C for 30 minutes. It was left standing for 24 hours, and then, the coating film was separated and extracted in acetone under reflux for 6 hours to determine a gel ratio (%) from the coating film weights before and after extraction according to the following  
20 equation:

$$\text{gel ratio (\%)} = \frac{\text{coating film weight after extraction}}{\text{coating film weight before extraction}} \times 100$$

25 Coating film hardness: the curing composition was applied on a tin plate by means of an applicator so that the cured film thickness was about 45  $\mu\text{m}$  and heated and dried at 140°C for 30 minutes to obtain a coated test plate. It was left standing for 24 hours, and then, a Knoop hardness of the coating film surface on the coated test plate was measured in a room of 20°C.

30 [0060]

Coloring of the coating film: a coloring degree of the coating film on the coated test plate used for evaluating the coating film hardness described above was visually evaluated. In the table, the term "none" shows that coloring is not observed and is good, and the term "brown" shows that the coating film is

[Table 1]

### Table 1

[illegible]

[0062]

[Table 2]

Table 1 (continued)

		Example						Comparative Example
		8	9	10	11	12	13	1
Kind of curing composition		A-8	A-9	A-10	A-11	A-12	A-13	B-1
Celoxide 2021P		100			80	80	80	100
Mixed solution (b-1) obtained in Synthetic Example 2			100					
Mixed solution (b-2) obtained in Synthetic Example 3				100				
Cardura E-10					20			
3-Ethyl-3-hydroxy-methyloxetane						20		
$\epsilon$ -Caprolactone							20	
$\text{Zn}(\text{OTf})_2$			0.5	0.5	0.5	0.5	0.5	
$\text{Mg}(\text{OTf})_2$								
$\text{Yb}(\text{OTf})_3$								
$\text{Gd}(\text{OTf})_3$		0.5						
$\text{Zn}(\text{BF}_4)_2$								1.0
Acrylic suspension stabilizer solution (a)		10	10	10	10	10	10	10
Newcol 504(25)								
Newcol 562SF		1						
Deionized water		36	37	37	37	37	37	37
Gel ratio (%)	100°C baking	78	90	90	70	82	72	0
	120°C baking	99	95	96	97	96	98	0
	140°C baking	100	98	99	99	98	98	0
Coating film hardness (KHN)		35	20	23	18	17	12	—
Coloring of coating film		None	None	None	None	None	None	None

[0063]

Wet-on-wet coating on water-based colored base coat

Preparation Example 1: preparation of coating composition for water-based colored base coat

5                   Mixed were 275 parts of the acrylic resin aqueous dispersion (c-1) having a non-volatile content of 20% obtained in Synthetic Example 4 described above, 40 parts of the acrylic resin aqueous solution (c-2) having a non-volatile content of 50% obtained in Synthetic Example 5 described above, 25 parts of "Cymel 350" (trade name, melamine resin, manufactured by Mitsui Cytec Co.,  
10   Ltd.), 20 parts of "Aluminum Paste AW-500B" (trade name, paste of aluminum powder which is a metallic pigment, manufactured by Asahi Kasei Metals Co., Ltd.), 20 parts of ethylene glycol monobutyl ether, and 253 parts of deionized water. Then, added thereto was "Thixol K-130B" (trade name, anti-sagging agent, manufactured by Kyoeisha Chemical Co., Ltd.) to control the viscosity so  
15   that it was 300 mPa·s (millipascal-second) with a B type viscometer (rotation speed of rotor: 6 rpm), whereby obtained was a coating composition (C-1) for a water-based colored base coat having a non-volatile content of about 19%.

[0064]

Examples 14 to 26 and Comparative Example 2

20                   An epoxy base cationically electrodepositable coating composition was electrodepositably applied on a dull steel plate having a thickness of 0.8 mm which was subjected to zinc phosphate chemical conversion treatment so that the dried coating film thickness was about 20  $\mu\text{m}$ . The coating film was baked at 170°C for 20 minutes and then rubbed with a sand paper of #400, and  
25   it was wiped with petroleum benzine for degreasing. Then, an intermediate coating surfacer for automobiles was applied thereon by means of an air spray so that the dried film thickness was about 25  $\mu\text{m}$ , and it was baked at 140°C for 30 minutes and then wet-rubbed with a sand paper of #400. It was drained and dried, followed by wiping with petroleum benzine for degreasing, whereby a  
30   material for testing was prepared.

[0065]

Then, the coating composition (C-1) for a water-based colored base coat obtained in the preparation example described above was applied on this

material so that the film thickness was 20  $\mu\text{m}$ , and it was dried (semi-cured) at 80°C for 5 minutes. Then, the curing compositions prepared in the respective examples and comparative examples described above which were controlled in a viscosity (viscosity: 30 seconds/Ford cup #4/20°C) were applied on the coated face thereof by wet-on-wet so that the film thickness was 40  $\mu\text{m}$  in terms of a cured coating film thickness, and both coating films were cured by heating at 140°C for 30 minutes.

[0066]

The coated test plates thus obtained were evaluated for a finish, coloring of the coating films, and a coating film hardness according to the following criteria.

[0067]

Finish: visually judged according to the following criteria.

- : smoothness, gloss, and sharpness are good, and nothing abnormal is observed
- Δ : any of smoothness, gloss, and sharpness is a little inferior
- X : any of smoothness, gloss, and sharpness is markedly inferior

[0068]

Coloring of the coating films: a coloring degree of the coating film was visually evaluated. In the following Table 2, the term "none" shows that coloring is not observed and is good, and the term "brown" shows that the coating film is colored brown and coloring is inferior.

[0069]

Coating film hardness: a Knoop hardness (20°C) of the coated face on the coated test plate was measured.

[0070]

[Table 3]

Table 2

Example No.	Example						
	14	15	16	17	18	19	20
Kind of curing composition	A-1	A-2	A-3	A-4	A-5	A-6	A-7
Finish	O	O	O	O	O	O	O
Coloring	None	None	None	None	None	None	None
Knoop hardness	25	24	24	23	26	26	24

[0071]

[Table 4]

Table 2 (continued)

Example No.	Example						Comparative Example
	21	22	23	24	25	26	2
Kind of curing composition	A-8	A-9	A-10	A-11	A-12	A-13	B-1
Finish	O	O	O	O	O	O	Uncured
Coloring	None	None	None	None	None	None	None
Knoop hardness	25	10	15	9	8	5	—

[0072]

[Effect of the invention]

As can be found from the examples, the curing composition of the present invention is a water-containing curing composition which is not colored in baking and can form a three-dimensionally cross-linked matter excellent in characteristics such as a hardness and a finish, and it is very useful for a water-based coating composition. According to the production method for a cured coating film of the present invention, a coating film which is not colored in baking and has good characteristics such as a hardness and a finish is obtained as well in coating by wet-on-wet.

[Document Name] Abstract

[Abstract]

[Subject]

The present invention provides a water-containing curing composition which is less liable to be influenced by coating environment and coating conditions, excellent in curing property at a low temperature without using a lot of a polymerization catalyst, and capable of forming a cured matter excellent in performances such as a hardness.

[Means for Solution]

A curing composition comprising:

(A) a polymerizable cyclic structure-containing component comprising a compound (a-1) having at least two polymerizable cyclic ether structures in a molecule and, if necessary, a compound (a-2) having one  
5 polymerizable cyclic structure in a molecule,

(B) 0.01 to 5 parts by weight of a metal triflate per 100 parts by weight of the above component (A), and

(C) 0.1 to 250 parts by weight of water,

wherein the above polymerizable cyclic structure-containing component (A) has  
10 a polymerizable cyclic structure equivalent (molecular weight/number of polymerizable cyclic structure in a molecule) falling in a range of 100 to 1,000 on average.

[Selected Drawing]

None

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